AQUEOUS GLITTERING INK

BACKGROUND OF THE INVENTION

Cross-Reference to Related Application

This application is a Continuation –In Part application of, and claims priority from, U.S.Patent application Serial No.09/523,619 entitled " AQUEOUS GLITTERING INK COMPOSITION" filed on March 13, 2000.

Field of the Invention

The present invention relates to an aqueous glittering ink which can be suitably used for writing tools, printing inks, fields pertaining to coatings, cosmetics, and the like.

Description of the Prior Art

Heretofore, for the purpose of obtaining written marks with metallic luster such as gold and silver, aqueous inks using glittering pigments have been proposed. For example, Japanese Unexamined Patent Publication Hei 7-118592 proposes an aqueous ink using an aluminum powder pigment. Japanese Unexamined Patent Publication Hei 8-151547 proposes an ink using a pearlescent pigment. Japanese Unexamined Patent Publication Hei 11-29734 proposes an aqueous metallic ink prepared by coloring an aluminum powder with an organic pigment fixed.

However, in the case of such conventional aqueous inks using glittering pigments such as aluminum powder pigment, pearlescent pigment and the like, it has been difficult to obtain written marks or coated films with strong

glittering feeling and spatial effect. Moreover, although in order to obtain, in particular, colored metallic color, a method has been adopted in which these glittering pigment particles are colored with coloring materials such as dyes and pigments, there has been a problem that the glittering feeling is lost despite the improvement in color development.

SUMMARY OF THE INVENTION

As a result of intensive studies for achieving the said objects, the present inventors have adopted an aqueous glittering ink containing scaly glittering particles, a water-soluble resin, a water-soluble organic solvent, a colorant and water, wherein the said scaly glittering particles have a median diameter of at least 10μm, a ratio of smoothness on the particle surface to a median diameter of not greater than 0.011, and a surface coating ratio of the said colorant on the said particle surface of not greater than 80% in a state of dried written marks.

By adopting the said constituents, written marks or coated films can be obtained with a strong glittering feeling and a spatial effect, as well as a good color development compared with the aqueous ink using the conventional glittering pigments.

In particular, as a preferred embodiment of this invention, in addition to the above-mentioned constituents, it is desirable to use an aqueous ink having the pseudo-plasticity fluidity (thixotropic property), preferably an aqueous ink having the said thixotropy index (T.I. value) of not less than 1.3 represented by the ratio of $V_{0.5}$ to $V_{1.0}$ ($V_{0.5}$ / $V_{1.0}$), wherein $V_{0.5}$ is the viscosity with the rotation speed of 0.5 rpm and $V_{1.0}$ is the viscosity with the

rotation speed of 1.0 rpm when the ink is measured by an ELD-typed viscometer (3° R14 cone, at the temperature of 20℃), more preferably an aqueous ink having the pseudo-plasticity fluidity (thixotropic property) with $V_{0.5}$ of 1000~15000mPa · s, preferably 1000~10000mPa · s, the viscosity when measured by an ELD-typed viscometer with a rotation speed of 0.5rpm(3° R14 cone at the temperature of 20℃).

By preparing the aqueous ink having the said constituents, even in the case of containing the scaly glittering particles with the said parameters having quite a large particle size compared with that of the normal coloring pigments, it is capable of controling the dispersal stability of the said particles in the ink and is capable of preventing the sedimentation of the scaly glittering particles. Therefore, even in the case of applying the ink of this invention to the ink for a ball-point pen, for example, it is capable of showing the excellent glittering feeling of the glittering particles and the strong color development of the colorants at a time, while showing the stability and good writing performance since it can prevent the clogging of the glittering particles with the said large particle diameters at the pen tip.

The object of this invention is to provide a glittering aqueous ink having a stronger glittering feeling and spatial effect and better color development than those achieved by an aqueous ink using conventional glittering pigments without losing a glittering feeling.

The other object of this invention is to provide a glittering aqueous ink capable of showing the glittering feeling of the glittering particles and the color development of the colorants at a time, while maintaining the stability

and good writing performance of the ink.

BRIEF DESCRIPTION OF DRAWING

Figure 1 is the schematic sectional view showing the typical example of written marks when writing with the ink by the said writing method.

DESCRIPTION OF THE PREFERRED EMBODIMENT

(Scaly glittering particles)

As the scaly glittering particles, it is important to have such particles having a median diameter of at least 10μm, a ratio of smoothness on the particle surface to a median diameter of not greater than 0.011, and a surface coating ratio of the said colorant on the particle surface of not greater than 80% in a state of dried written marks.

The "glittering particles" in this invention refer to the particles which realize the glittering feeling on dried written marks or coated films, more concretely, referring to those particles with the said parameters.

Here, the said "median diameters" are the D_{50} value (μm) measured by laser diffraction analysis using an equipment manufactured by Leeda & Northlup under the trade name of "Microtrac HRA 9320-X100". In addition, the said smoothness is the average value of R_{max} (μm), the maximum value of roughness measured on each surface of the several glittering particles which exist per unit area of the written marks or coated films in a state of dryness by using the electron microscope manufactured by ELIONIX INC. under the trade name of "ERA-8000".

According to this invention, when the ink is written or coated and forms the written marks or coated films, in such written marks or coated films, the

larger the median diameters of the D_{50} value, and the smaller the R_{max}, the maximum value of the said roughness on the surface, the stronger glittering feeling can be realized. Further, the inventors have found that, when the minimum value of the glittering feeling to which both parameters relate is associated as the ratio of the smoothness (μm) on the particle surface to the said median diameter (μm) of the glittering particles (smoothness (μm) / median diameter (μm)), the realization of the glittering feeling is related to the said ratio, in particular, when the ratio is not grater than 0.011, the glittering feeling is strongly realized.

Further, as above mentioned, it is important for the glittering particles in the present invention to have a surface coating ratio of the said colorant on the particle surface of not greater than 80% in a state of dried written marks. Here, the "surface coating ratio of the colorant" refers to the coating ratio of the colorant including the coloring pigment which covers the surface of a particle and is represented by the coating area of the colorant to the total surface area of the surface of a particle. In the present invention, the coating ratio of the colorant is so obtained as using the electron microscope manufactured by ELIONIX INC. under the trade name of "ERA-8000" as already mentioned, and measuring the average value of the surface area of the said particles and the coating area of the colorant on the several glittering particles existing per area in the written marks or coated films. This "surface coating ratio of the colorant" is the parameter capable of the adjustment, depending on the size , and contained amount of the glittering

particles and colorant's particles, dispersability of each particle in the ink, and the viscosity of the ink.

In the case of an aqueous ink wherein the median diameter of the scaly glittering particles is less than 10μm, a glittering feeling on the written marks or coated films lowers. Even in the case of an aqueous ink wherein the median diameter of the scaly glittering particles is not less than 10μm, when the ratio of smoothness on the particle surface to the said median diameter exceeds 0.011, a glittering feeling on the written marks or coated films also lowers. In the case of an ink wherein the surface coating ratio of the said colorant coating the surface of the said scaly glittering particles in written marks and coated films marks exceeds 80%, a glittering feeling also lowers. For information, in the case of the scaly glittering particles whose median diameter is at least 25μm, preferably not less than 30μm the excellent glittering feeling appears in written marks or coated films.

In the present invention, examples of the glittering particles capable of having the said parameter include the glass flake particles and the metal coated inorganic particles. Here, the glass flake particles are defined as particles wherein a flaky glass is coated with a metal and the like. And the metal coated inorganic particles are defined as a general term of inorganic particles coated with a substance, at least either one of a metal or a metallic oxide.

The aqueous ink containing such particles as having a median diameter of at least 10μm, the ratio of smoothness on the particle surface to the said median diameter of not greater than 0.011, and the surface coating ratio of

the said colorant on the particle surface of not greater than 80% in a state of dried written marks is capable of forming written marks or coated films with a glittering feeling and a spatial effect which the glittering particles originally have and the good color development which the colorants have.

As an example of glass flake particles, a glass flake particles formed of a flaky glass coated with metal by electroless plating can be used. For example, ones coated with silver available from Toyo Aluminium Co., Ltd. under the trade names of "Metashine REFSX-2015PS", "Metashine REFSX-2025PS" and "REFSX-2040PS" can be mentioned.

In addition, glass flake particles formed of a flaky glass coated with metal by spattering can also be used. For example, ones coated with silver available from Toyo Aluminium Co., Ltd. under the trade names of "Crystal Color GF2125", "Crystal Color GF2125-M", "Crystal Color GF2140" and "Crystal Color GF2140-M" can be mentioned. Also ones coated with nickel-chromium-molybdenum available from the same company under the trade names of "Crystal Color GF2525", "Crystal Color GF2525-M", "Crystal Color GF2540" and "Crystal Color GF2540-M" can be mentioned. Also, one coated with brass available from the same company under the trade name of "Crystal Color GF250", one coated with silver alloy available from the same company under the trade name of "Crystal Color GF1345", and one coated with titanium available from the same company under the trade name of "Crystal Color GF1445" can be mentioned.

In addition, as an example of metal coated inorganic particles to be used in the present invention, aluminum coated with iron(III) oxide can be used. For example, ones available from BASF AG under the trade names of

"Paliocrom Gold L2000", "Paliocrom Gold L2002", "Paliocrom Gold L2020", "Paliocrom Gold L2022", "Paliocrom Gold L2025", and "Paliocrom Orange L2800" can be mentioned. In addition, mica coated with iron(III) oxide can also be used. For example, ones available from BASF AG under the trade names of "Paliocrom Red Gold L2500" and "Paliocrom Red L4000" can be mentioned. Moreover, mica-like iron(III) oxide coated with aluminum-manganese can be used. For example, ones available from BASF AG under the trade names of "Paliocrom Copper L3000" and "Paliocrom Copper L3001" can be mentioned. Mica coated with reduced titanium dioxide can also be used. For instance, ones available from BASF AG under the trade names of "Paliocrom Blue Silver L6000" and "Paliocrom Blue Silver L6001" can be mentioned. Moreover, mica coated with titanium dioxide can also be used.

Further, aluminum powders, as far as they are the scaly glittering particles having a median diameter of at least 10μm, a ratio of smoothness on the particle surface to the said median diameter of not greater than 0.011, and a surface coating ratio of the said colorant on the particle surface of not greater than 80% in a state of dried written marks as above-mentioned, the color development of the colorant can be realized while maintaining the starry glitter on the written marks or coated films which the particles originally have.

The examples of such aluminum powders capable of providing the said parameter include the ones manufactured by Toyo Aluminium under the trade name of "WXM U75C"(median diameter: 13 μm), "WXM 5422"(median diameter: 18 μm), "WXM 1440"(median diameter: 30 μm), and "WXM 1415"(median diameter: 50 μm). In particular, as aluminum powders,

"WXM 1440"(median diameter: 30 μm), and "WXM 1415"(median diameter: 50 μm) whose median diameter is not less than 30 μm, that is, with a median diameter exceeding 25μm can preferably be used.

Here, it is important for the said scaly glittering particles including these glass flake particles and metal coated inorganic particles to have a median diameter of at least 10 μm, preferably not less than 25μm and most preferably not less than 30 μm. It is preferable to have a median of 100μm at the maximum. The case in which the median diameter exceeds 100 μm is unfavorable because it does not come out of the pen tip easily when used as an ink for ball-point pens.

In addition, in the aqueous ink of the present invention, the said scaly glittering particles including glass flake particles and metal coated inorganic particles are preferably contained in 0.01 - 40% by weight relative to the total amount of the ink. When the content of the said scaly glittering particles is less than 0.01% by weight relative to the total amount of the ink, the glittering feeling becomes unsatisfactory. When the content of the said scaly glittering particles exceeds 40% by weight relative to the total amount of the ink, the viscosity of the ink becomes so high that the fluidity is reduced. The optimum content of the said scaly glittering particles ranges from 0.5 - 30% by weight.

(Water-soluble organic solvent)

Water-soluble organic solvents capable of preventing both drying at the pen tip of a ball-point pen and freezing of the ink are preferably used, which can be exemplified by glycols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol and polyethylene glycol, polyhydric

alcohols such as glycerin, glycol ethers such as ethylene glycol monomethyl ether, diethylene glycol monomethyl ether, dipropylene glycol monomethyl ether and dipropylene glycol monopropyl ether. These organic solvents may be used alone or in combinations of two or more of them.

The content of the water-soluble organic solvent is preferably contained in 1.00 - 40% by weight relative to the total amount of the ink. When the content of the water-soluble organic solvent is less than 1.00% by weight relative to the total amount of the ink, the pen tip becomes susceptible to dry and the ink becomes liable to freeze. When the content of the water-soluble solvent exceeds 40% by weight relative to the total amount of the ink, written marks or coated films is difficult to dry out as well as solubility of the water-soluble resin being influenced. The optimum content of the water-soluble organic solvent, which varies depending on its type, ranges from 5.00 - 20% by weight.

(Colorant)

A colorant can be used in the present invention. The use of a colorant can adjust the ink colors to a variety of colors. It is important that such a colorant should be used as does not react with the said scaly glittering particles nor does it influence the color development (glittering feeling) of such scaly glittering particles. Moreover, colorants with high solubility and dispersibility are favorable.

Examples include water-soluble dyes such as acid dyes, direct dyes and basic dyes, inorganic pigments such as carbon black and titanium oxide, organic pigments such as copper phthalocyanine pigments, threne pigments, azo pigments, quinacridon pigments, anthraquinone pigments, dioxane

pigments, indigo pigments, thioindigo pigments, perinone pigments, perylene pigments, indolenone pigments and azomethine pigments, and fluorescent pigments, colored resin emulsions and the like can be mentioned. These also may be used in the form of a pigment dispersion. The present invention can use one species of pigment or can use two or more species of pigments in combination. In addition, several scaly glittering particles relating to this invention can be mixed and used. Further, the scaly glittering particles relating to this invention and the conventional glittering pigments can be mixed and used. For example, the glass flake particles, metal coated inorganic particles, aluminum powder pigments, and pearlescent pigments and the like can be mixed. Furthermore, they can be mixed with opacifying pigments including a variety of inorganic or organic white pigments such as titanium oxide, alkylene bismelamine derivatives, plastic pigments (synthetic resin particle pigments) with opacifying power of various shapes including spherical shapes, oblate shapes and the like. The metal coated inorganic pigment also can be used together with the glass flake pigment.

Such a colorant need not be contained in the aqueous ink of the present invention. Even aqueous inks containing not colorants but glass flake pigments or metal coated inorganic pigments can provide high glittering feeling and high spatial effect to written marks or coated films. Also even aqueous inks not containing colorants but containing metal coated inorganic pigments can add high glittering feeling to written marks or coated films. The said aqueous inks containing colorants, however, are extremely preferable because they can provide a colored strong glittering feeling

depending upon the hue or the like of the colorants contained.

The colorant is preferably contained in 0.01 - 30% by weight relative to the total amount of the ink. When the colorant is less than 0.01% by weight relative to the total amount of the ink, coloring by the colorant is difficult to be visually recognized. When the colorant exceeds 30% by weight in the total amount of the ink, the viscosity of the ink becomes so high that the fluidity becomes poor. The optimum amount of the colorant to be compounded, which varies depending on its type, ranges from 0.05 - 20% by weight.

(Water-soluble resin)

As a water-soluble resin, preferably used is the water-soluble thickening resin which is capable of dispersing the scaly glittering particles and of preventing them from precipitation. In particular, in order to make a coating ratio of a colorant to the written marks of the said scaly glittering particles not greater than 80%, it is important to adjust the dispersion of the scaly glittering particles and the pigment particles and to adjust the viscosity of the said and as-will-be-seen pseudo-fluidity property (thixotropic property) respectively as a measure, and in this sense, it is important to contain this water-soluble resin in the ink.

Applicable as polysaccharides are microbial polysaccharides and derivatives thereof, including pullulan, xanthan gum, welan gum, rhamsan gum, succinoglucan and dextran; water-soluble polysaccharides derived from plants and derivatives thereof including tragacanth gum, guar gum, tara gum, locust bean gum, ghatti gum, arabinogalactan gum, gum arabic, quince seed gum, pectin, starch, psyllium seed gum, pectin, carrageenan, alginic

acid , agar and the like; water-soluble polysaccharides derived from animals and derivatives thereof including gelatin, casein and albumin. Moreover, N-vinylacetamide type resins such as N-vinylacetamide resin and crosslinked N-vinylacetamide resin can be used as the thickening resin.

In the present invention, the microbial polysaccharides and derivatives thereof can specifically and preferably be used among the said water-soluble resins. Such water-soluble resins can be used either alone or in combinations of two or more of them.

The water-soluble resin is preferably contained in 0.01 - 40% by weight relative to the total amount of the ink. If the content of the water-soluble resin is less than 0.01% by weight relative to the total amount of the ink, effect on preventing precipitation of the scaly glittering particles including glass flake particles, metal coated inorganic particles and the like becomes unsatisfactory. When the water-soluble resin exceeds 40% by weight relative to the total amount of the ink, the viscosity of the ink becomes so high that the fluidity becomes poor. The optimum amount of the water-soluble resin to be compounded, which varies depending on its type, ranges 0.05 - 20% by weight.

(Synthetic resin emulsion)

As previously mentioned, the present inventors have found that in order to obtain written marks of metallic luster color such as gold and silver and the like, the use of scaly glittering particles having a median diameter of at least 10 μm, a ratio of smoothness on the particle surface to a median diameter of not greater than 0.011, and a surface coating ratio of the said colorant in written marks of not greater than 80% together with the use of a

colorant is preferable. The scaly glittering particles can provide, to written marks or coated films, glittering feeling and spatial effect higher than those with the conventional aluminum powder pigments and pearlescent pigments as well as providing the clear color development of the colorant.

However, they have also found that although an aqueous glittering ink containing a water-soluble thickening resin can increase the fixability of the glittering particles including glass flake pigments and the like by this water-soluble thickening resin, it is difficult to fix firmly the glittering particles including glass flake particles and the like to written marks or coated films since the size of the scaly glittering particles is large having the median diameter of not less than 10 μm, preferably not less than 25 μm, and more preferably not less than 30 μm. Accordingly, in the case of the aqueous ink containing glittering particles including glass flake particles, the glittering particles including glass flake pigments and the like are easily peeled by friction after writing or coating and it is difficult to maintain high glittering feeling and spatial effect to written marks or coated films. Therefore, the durability of written marks or coated films having glittering feeling and spatial effect becomes poor.

From the above-mentioned situation, an important problem is to provide aqueous glittering inks which can improve the fixability of glittering particles including glass flake particles and the like to written marks or coated films and maintain a higher glittering feeling and spatial effect for the written marks or coated films without deteriorating ink characteristics or writing characteristics and without inhibiting the effects on the high glittering feeling and spatial effect derived from compounding the glittering

particles including glass flake particles and the like.

As a result of intensive studies for solving this problem, they have found that the problem can be solved by aqueous glittering inks containing glittering particles, a water-soluble thickening resin, a water-soluble organic solvent and water, and further containing a binder component which fixes the glass flake pigment to written marks or coated films.

On the other hand, another possible option for fixing such glittering particles to written marks or coated films is to use a water-soluble synthetic resin as a binder component. However, in the case of some water-soluble synthetic resins, if the contents thereof are set to be high in order to firmly fix the glittering particles with a large particle diameter as in the present invention, the solubility of the thickening resin and dispersibility of the colorant are badly influenced. Moreover, there may be cases where viscoelasticity of the ink are greatly reduced, which leads to reduction in writing characteristics. Moreover, even if fixability to written marks or coated films is shown, aqueous inks should not be the ones wherein high glittering feeling and spatial effect of the glittering particles are contained but are poor in written marks or coated films.

The present inventors have made further intensive studies. As a result, they have found that the use of a synthetic resin emulsion as a binder component for fixing the glittering particles to written marks or coated films permits improvement in fixability of the glittering particles to written marks or coated films without influencing the solubility of water-soluble thickening resins, dispersibility of colorants, viscoelasticity of ink, and coloring of ink and without inhibiting effects of high glittering feeling and spatial effect by

compounding the glittering particles, and they have accomplished the present invention.

Accordingly, the aqueous ink of the present invention which contains a glittering particles with a large particle size is capable of improving the fixability of the glass flake pigment to written marks or coated films, forming written marks or coated films of durability, and maintaining a high glittering feeling and spatial effect for the written marks or coated films when it is put on a substrate such as paper, metal, plastics and textile fabrics by writing or coating. The reason for this is that the film formability of the synthetic resin emulsion is suitable for glittering particles including glass flake particles having a large-sized particle shape and the glittering particles can be fixed firmly to written marks or coated films without inhibiting the effects of high glittering feeling and spatial effect by compounding the glittering particles

Moreover, since the binder component used in the present invention is not a water-soluble synthetic resin but a synthetic resin emulsion, it does not influence properties including solubility of the water-soluble thickening resin to be compounded together, dispersibility of the colorant and viscoelasticity of the ink very much. The ink of the present invention therefore can improve the fixability of the glittering particles without influencing the viscoelasticity of the ink, writing characteristics and color of written marks or coated films.

From such facts, the aqueous glittering ink of the present invention containing the glittering particles can maintain, in written marks or coated films, a glittering feeling and spatial effect higher than those achieved by the

conventional aqueous inks using glittering pigments such as aluminum powder pigments and pearlescent pigments without deteriorating ink characteristics, writing performance or the like or without inhibiting the high surface smoothness inherent to glass.

The synthetic resin emulsion of the present invention is not specifically limited and any water-dispersive synthetic resin emulsion is available. Considering the ink characteristics and writing performance however, it is important to use the ones which do not influence solubility of water-soluble thickening resin, viscosity of the ink, dispersibility of the colorant and coloring of the ink. Moreover, it is important not to inhibit the effect on the high glittering feeling and spatial effect caused by the composition of the glittering particles including glass flake particles and the like.

The minimum film forming temperature of the synthetic resin emulsion is preferably not higher than 20°C. If the minimum film forming temperature of the synthetic resin emulsion is not higher than 20°C, particularly not higher than 0°C, a film can be formed not only at room temperature (about 25°C) but in a cold district and fixability of written marks or coated films to substrates can be improved.

Synthetic resin emulsions having an anionic property or a nonionic property preferably can be used. Such synthetic resin emulsions having the anionic property or the nonionic property can be prepared, for example, by producing synthetic resins from anionic or nonionic monomers or using anionic or nonionic emulsifiers. If the synthetic resin emulsion has the anionic property or the nonionic property, the stability of the ink can be improved.

Preferred synthetic resin emulsions do not influence the dispersibility of colorants or solubility of water-soluble thickening resin when the pH of inks is 6 or more.

From such a viewpoint, for example, acryl based synthetic resin emulsions, styrene-acryl based synthetic resin emulsions and vinyl acetate based synthetic resin emulsions can be used as a synthetic resin emulsion. Preferred examples of the acryl based synthetic resins include acrylate copolymer synthetic resin emulsions. Preferred examples of the styrene-acryl based synthetic resin emulsions include styrene-acrylate copolymer synthetic resin emulsions. As the vinyl acetate based synthetic resin emulsions, vinyl acetate synthetic resin emulsions and vinyl acetate-acrylate copolymer synthetic resin emulsions, for example, are preferably used. As the synthetic resin emulsion, one species of these synthetic resins can be used and also two or more species of these synthetic resins can be used in combination.

For example, the acryl based synthetic resin emulsion can be exemplified by the trade name "Nikasol FX336" (manufactured by Nippon Carbide Industries Co., Inc.; anionic; pH 7.5; minimum film forming temperature = 0℃), the trade name "Mowinyl DM772" (manufactured by Clariant Polymers Co., Ltd ; anionic; pH 8.5; minimum film forming temperature = 12 – 14℃) and the trade name "Mowinyl 700" (manufactured by Clariant Polymers Co., Ltd ; anionic; pH 8.0; minimum film forming temperature = 5℃). The vinyl acetate based synthetic resin emulsion can be exemplified by the trade name "Nikasol TG134A" (manufactured by Nippon Carbide Industries Co., Inc.; pH 7.5; minimum film forming temperature = 0

°C) and the trade name "Mowinyl 507" (manufactured by Clariant Polymers Co., Ltd ; nonionic; pH 6.5; minimum film forming temperature = 0°C).

Although the content of the synthetic resin emulsion is not particularly specified, a preferable range is 0.01 - 40% by weight in solids relative to the total amount of the ink, for example. The content of the synthetic resin emulsion of less than 0.01% by weight in solids relative to the total amount of the ink results in reduction in fixability of the glittering particles including glass flake particles to written marks or coated films. If the content of the synthetic resin emulsion exceeds 40% by weight in solids relative to the total amount of the ink, the solids are so high that writing characteristics are deteriorated because of, for example, film formation at the pen tip. In addition, written marks or coated films are liable to whiten. In order to improve the fixability of the glittering particles including glass flake particles and the like to written marks or coated films further, the most desirable content of the synthetic resin emulsion is at least 0.3% by weight in solids relative to the total amount of the ink. Moreover, in order to improve writing characteristics further, the most desirable content of the synthetic resin emulsion is 20% by weight in solids relative to the total amount of the ink. That is, the optimum content of the synthetic resin emulsion is 0.3 - 20% by weight .

In addition, also in the case of the ink containing the synthetic resin emulsion as a binder component together with the glittering particles including glass flake particles, it is important that the resins can adjust viscosity of the ink and facilitate dispersion of the glass flake pigment and prevent its precipitation. Water-soluble thickening resin with a function to

form a film of written marks or coated films can be used. For example, microbial polysaccharides and derivatives thereof can be used, including pullulan, xanthan gum, welan gum, rhamsan gum, succinoglucan and dextran. Water-soluble polysaccharides derived from plants and derivatives thereof also can be used, including tragacanth gum, guar gum, tara gum, locust bean gum, ghatti gum, arabinogalactan gum, gum arabic, quince seed gum, pectin, starch, psyllium seed gum, pectin, carrageenan, alginic acid and agar. Water-soluble polysaccharides derived from animals and derivatives thereof can also be used, including gelatin, casein and albumin.

As the water-soluble thickening resin, salts (sodium salts, ammonium salts and the like) of water-soluble resins (acryl based water-soluble resins, styrene-acryl based resins, styrene-maleic acid based resins and the like), water-dispersion type resins and the like can also be used.

In the case of inks which contain a synthetic resin emulsion as a binder component together with the glittering particles including glass flake particles and the like, the microbial polysaccharides and derivatives thereof can be used preferably among the said water-soluble thickening resins. Such water-soluble thickening resins can be used either alone or in combinations of two or more of them.

In the case of inks which contain a synthetic resin emulsion as a binder component together with the glittering particles including glass flake particles, the water-soluble thickening resin is preferably contained in 0.01 - 40% by weight relative to the total amount of the ink. In the case where the water-soluble thickening resin is less than 0.01% by weight relative to the

total amount of the ink, the glittering particles including glass flake particles are liable to precipitate. If the water-soluble thickening resin exceeds 40% by weight relative to the total amount of the ink in the case of the ink containing the synthetic resin emulsion, the viscosity of the ink becomes so high that the fluidity becomes poor and writing characteristics are deteriorated. The optimum amount of the water-soluble thickening resin to be compounded somewhat varies depending upon the type of the water-soluble thickening resin, but is 0.05 - 20% by weight.

Also in the case of the ink containing a synthetic resin emulsion as a binder component together with the glittering particles including glass flake particles and the like, water-soluble organic solvents which are capable of preventing both drying at the pen tip and freezing of the ink are preferably used, which can be exemplified by glycols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol and polyethylene glycol, polyhydric alcohols such as glycerin, and glycol ethers such as ethylene glycol monomethyl ether, diethylene glycol monomethyl ether, dipropylene glycol monomethyl ether and dipropylene glycol monopropyl ether, and the like. These organic solvents can be used either alone or in combination of two or more of them.

As for water-soluble organic solvents, aliphatic monohydric alcohols with 1 to 4 carbon atoms, aliphatic polyhydric alcohols such as glycerin, glycols such as propylene glycol and glycol ethers such as propylene glycol monomethyl ether and the like are preferably used.

Also in the case of the ink containing the synthetic resin emulsion as a binder component together with the glittering particles including glass flake

particles and the like, the content of the water-soluble organic solvent is 1 - 40% by weight relative to the total amount of the ink. In the case where the content of the water-soluble organic resin is less than 1% by weight relative to the total ink, a pen tip is liable to dry and the ink becomes liable to freeze. If the content of the water-soluble organic solvent exceeds 40% by weight relative to the total amount of the ink, the solubility of the water-soluble thickening resin is influenced and written marks and coated films become hard to dry. In the case of this ink, the optimum amount of the water-soluble organic solvent to be compounded varies depending upon the type of the water-soluble organic solvent, but is 5 - 30% by weight.

Also in the case of the ink containing the synthetic resin emulsion as a binder component together with the glittering particles including glass flake particles and the like, colorants can be used. The use of colorants can adjust the color of the ink to various colors. It is important to use colorants which do not react with the glittering particles including glass flake particles and do not influence the coloring of the glittering particles including glass flake particles. Moreover, the one excellent in solubility and dispersibility are preferable as a colorant.

For example, water-soluble dyes such as acid dyes, direct dyes and basic dyes (triphenylmethane-type, xanthene-type, anthraquinone-type, metal complex-type, copper phthalocyanine-type and the like), organic pigments or inorganic solvents such as phthalocyanine, quinacridone, carbon black and titanium oxide, or fluorescent pigments, resin emulsions, colored resin emulsion and the like can be used. The colorant also can be compounded in the form of a pigment dispersion. The colorants can be used either alone or

in combinations of two or more of them.

Also in the case of the ink containing the synthetic resin emulsion together with the glittering particles including glass flake particles and the like, colorants need not be contained. Even aqueous inks containing not colorants but the glittering particles including glass flake particles can add a high glittering feeling and high spatial effect to written marks or coated films. Each of the said aqueous inks containing colorants, however, is extremely preferable because they can provide high brilliance depending upon the hue or the like of the colorants contained.

In the case of the ink containing the synthetic resin emulsion as a binder component together with the glittering particles including glass flake particles, the content of the colorant is preferably 0.01 - 30% by weight relative to the total amount of the ink. When the colorant is less than 0.01% by weight relative to the total amount of the ink, the coloring by the colorant becomes difficult to be visually recognized. When the colorant exceeds 30% by weight relative to the total amount of the ink, the viscosity of the ink becomes so high that the fluidity becomes poor and glittering feeling is deteriorated. The optimum amount of the colorant to be compounded, which varies depending on its type, is 0.05 - 20% by weight.

(Viscosity range)

The viscosity range is not specifically limited but such an aqueous ink is preferable as mentioned above, having the pseudo-plasticity fluidity (thixotropic property) whose thixotropy index (T.I. value) is not less than 1.3 represented by the ratio of $V_{0.5}$ to $V_{1.0}$ ($V_{0.5}$ / $V_{1.0}$), wherein $V_{0.5}$ is the viscosity with the rotation speed of 0.5 rpm and $V_{1.0}$ is the viscosity with the

rotation speed of 1.0 rpm when the ink is measured by an ELD-typed viscometer (3° R14 cone, at the temperature of 20°C). Further, the aqueous ink having the pseudo-plasticity fluidity (thixotropic property) with $V_{0.5}$ of 1000~15000mPa · s, the viscosity when measured by an ELD-typed viscometer with a rotation speed of 0.5rpm(3° R14 cone at the temperature of 20°C) is preferable.

In addition, such an aqueous ink is preferable as having the pseudo-plasticity fluidity (thixotropic property) whose thixotropy index (T.I. value) is not less than 1.3 represented by the ratio of $V_{0.5}$ to $V_{1.0}$ ($V_{0.5}$ / $V_{1.0}$), wherein $V_{0.5}$ is the viscosity with the rotation speed of 0.5 rpm and $V_{1.0}$ is the viscosity with the rotation speed of 1.0 rpm when the ink is measured by an ELD-typed viscometer (3° R14 cone, at the temperature of 20°C) and having the pseudo-plasticity fluidity (thixotropic property) with $V_{0.5}$ of 1000~15000mPa · s, the viscosity when measured by an ELD-typed viscometer with a rotation speed of 0.5rpm(3° R14 cone at the temperature of 20°C).

Here, when $V_{0.5}$, the viscosity with the rotation speed of 0.5 rpm measured by an ELD-typed viscometer (3° R14 cone, at the temperature of 20°C) is less than 1000mPa · s, since the viscosity is low in the case of the ink containing the said glittering particles relating to the present invention, the dispersal stability lowers, thereby causing precipitation over time and it is not preferable. On the other hand, when $V_{0.5}$ exceeds 15000mPa · s, the viscosity becomes so high that the writing characteristics lowers particularly when used as the ink for ball-point pens.

(Other additives)

Moreover, to the ink of the present invention can be compounded conventional water such as ion-exchange water. In addition, as needed, lubricants such as polyoxyethylene alkali metal salts, dicarboxylic amides, phosphates and N-oleyl sarcosine salts and the like, rust-inhibitors such as benzotriazole and tolyltriazole dicyclohexyl ammonium nitrate and the like, antiseptic mildew-proofing agents such as benzoisothiazoline-type, pentachlorophenol-type and cresol and the like, and various surfactants can be added.

(Applications)

The aqueous glittering ink can be used in the fields of writing tools, printing, coating and cosmetics and the like. It is useful in a variety of applications as an aqueous glittering ink for writing tools (an aqueous glittering ink for ball-point pens and the like), an aqueous glittering ink for printing, an aqueous glittering ink for applicators (an aqueous glittering ink for coating and the like) and the like. It is particularly the most desirable as an aqueous glittering ink for ball-point pens.

(Method of preparation)

The aqueous glittering ink of the present invention is not specifically limited but can be obtained, for example, by mixing and stirring ingredients such as water, a water-soluble organic solvent, a glass flake pigment and a colorant or a pigment base to disperse them, and thereafter charging a water-soluble resin and filtering the resulting mixture, and subsequently degassing. In particular, the ink containing the synthetic resin emulsion as

a binder component together with the glittering particles is preferably prepared by the following process, although the preparation is not specifically limited. First, water, a water-soluble organic solvent, and, as needed, other additives are mixed and stirred; to the mixture is charged the glass flake pigment, and the resulting mixture is stirred; and thereafter a water-soluble thickening resin is added and stirred. Next, the pH of the mixed liquid is adjusted as needed, and a colorant is added and stirred, as needed. Subsequently, the synthetic resin emulsion is added and mixed.

As for these preparations, heretofore known dispersing techniques, degassing techniques, filtering techniques and the like can be adopted.

(Method of forming the written marks and the written marks)

The method of forming the written marks of the aqueous ink in the present invention is not specifically limited, but such a writing method of the aqueous glittering ink is preferable as having scaly glittering particles with a median diameter of at least 10μm, a ratio of smoothness on the particle surface to the said median diameter of not greater than 0.011, and a surface coating ratio of the said colorant on the particle surface of not greater than 80% in a state of dried written marks, wherein the said scaly glittering particles are interspersed with a rate of not greater than 80% with respect to the total written surface and the said colorant's particles are interspersed among the said glittering particles.

Figure 1 is the schematic sectional view showing the typical example of written marks when writing with the ink by the said writing method. As shown in Figure 1, in the embodiment of the present invention, the glittering particles 101 having the said property value are interspersed with the rate of

not greater than 80% with respect to the written surface10 on the surface of a sheet of paper 2 (a coated surface) and are capable of forming written marks 1 in which colorant's particles 103 are interspersed among glittering particles 101 and glittering particles 102. In written marks 1, when seen in a microscopic manner, the glittering particles 101 and 102 having the said property value are set on a sheet of paper 2 (coated surface) maintaining the smooth surface to the concavo-convex surface constituting the said coated surface, further among the glittering particles 101 having this smooth surface and glittering particles 102 having this smooth surface , the colorant's particles 103 are interspersed as a particle group partially absorbed in a tissue of a sheet of paper 2. In the embodiment of the present invention, written marks are shown by the two types of glittering particles 101 and 102. As a matter of course, however, it is important to make such written marks wherein several glittering particles exist and the colorants are interspersed among glittering particles having the said property value and the particle group of the colorants are arranged. By adopting such writing method or forming method of the written marks, the glittering particles have several smooth areas with a variety of angles interspersed on the surface of written marks due to the concavo-convex surface constituting the surface of a sheet of paper 2 (a coated surface). Moreover, since these glittering particles are the scaly glittering particles wherein the surface coating ratio of the said colorant on the particle surface is not greater than 80% in a state of dried written marks, there is little or no incidence of the light to the colorant's particles covering the surface of glittering particles 101 and 102. Therefore, without disturbing the reflected light to the respective smooth

surfaces of the glittering particles, the incident light 31 and reflected light 32 of light 3 can be obtained depending on the smooth surface of the glittering particles. Moreover, as shown in the Figure 1, since the incident light 31 and reflected light 32 of light 3 occur at a different angle to the respective smooth surfaces 111 and 112 of the glittering particles 101 and 102, by subtly changing the angle at which the written marks are seen at the eye's position the starry glitter is to be realized. Further, since the embodiment of the present invention refers to the written marks wherein the glittering particles having the said property value are interspersed with the rate of not greater than 80% to the total written surface area on the surface of a sheet of paper (a coated surface) and the colorant's particles are interspersed among the glittering particles, the glittering feeling of the glittering particles and the color development of the colorant are maintained with good balance thereby providing the starry glitter and color development with each other synergistically. Here, when the glittering particles having the said property value are interspersed with the rate of exceeding 80% to the total written surface on a sheet of paper (a coated surface), even there are colorants existing among the several glittering particles, the color development of the said colorants is suppressed since the glittering feeling of the glittering particles exceeds the color development of the colorants on the written surface. Besides, the glittering feeling of the glittering particles appearing on the written surface is not determined visually, solely by the area in which the glittering particles occupy on the written surface, but rather, if these glittering particles occupy most of the total written surface, together with the lowering of the color development of the colorant's particles,

the coloring surface of the glittering particles is to be formed and the glittering feeling lowers on the contrary. In other words, since the glittering feeling of the glittering particles is the visual feeling appearing synergistically in relation to the interspersion of the colorants existing among the glittering particles, it is also preferable to intersperse this glittering feeling with the rate of not greater than 80% to the total written surface in relation to the color development of the colorants. Here, in the present invention, the " interspersing rate" refers to the value (%) obtained by measuring the area of the glittering particles occupying the total written surface by using the microscope manufactured by ELIONIX INC. under the trade name of "ERA-8000" as already mentioned, thereby calculating the ratio. Here, it is more preferable for the scaly glittering particles of the present invention to be the particles wherein the surface coating ratio of the colorant on the particle surface is not greater than 40% in the state of dried written marks. In addition, it is the most suitable to intersperse these scaly glittering particles with the rate within the range of 20~45% to the total written surface.

By the way, the inventors have found that in the case of an aqueous ink which contains binder components fixing the said scaly glittering particles to written marks or coated films, while the resin component constituting the binder component fixes the scaly glittering particles to a written surface (a coated surface), it forms the resin film, directly covering the surface of the said glittering particles and that the resin film further forms the concavo-convex, which impairs the glittering feeling of the glittering particles. The preferred embodiment of the present invention has found that when the

concavo-convex rate which the resin film has is not greater than 0.15μm, the written marks can have a strong glittering feeling. In the present invention, the concavo-convex rate refers to the average value of R_{max} (μm), the maximum value of roughness measured on each surface of the several glittering particles which exist per unit area of the written marks or coated films in a state of dryness by using the microscope manufactured by ELIONIX INC. under the trade name of "ERA-8000".

The glittering feeling of this scaly glittering particles is realized well with the starry glitter when the rate of the smoothness on the coated film (the smoothness on the written surface) is not less than 9μm. When the rate of the smoothness on the coated film (the smoothness on the written surface) is less than 9μm, as above-mentioned, the gradient of the smooth surface of the glittering particles arranged on the written surface becomes small thereby making it difficult to receive the satisfactory starry glitter by changing the position to see these particles. Here, the "smoothness on the coated films" refers to the average value of R_{max} (μm), the maximum value of roughness measured on each surface of the several glittering particles which exist per unit area of the written marks or coated films in a state of dryness by using the microscope manufactured by ELIONIX INC. under the trade name of "ERA-8000".

EXAMPLES

Aqueous glittering inks of the Examples and Comparative Examples provided by mixing and stirring ingredients including water, a water-soluble organic solvent, glittering particles and a colorant or a pigment base and the like in the compositions and amounts (parts by weight) given in Table 1 to

disperse them, thereafter charging a water-soluble resin and filtering the resulting mixture, and subsequently degassing. In every preparation, heretofore known dispersing, degassing, filtering techniques and the like were used.

Likewise, aqueous glittering inks of other Examples and Comparative Examples were prepared by mixing and stirring ingredients including water, a water-soluble organic solvent, glittering particles, and the like in the compositions and amounts (parts by weight) given in Table 2 to disperse them, thereafter charging a water-soluble resin and filtering the resulting mixture, and subsequently degassing. In every preparation, heretofore known dispersing, degassing, filtering techniques and the like were used.

In the same manner as previously mentioned, aqueous glittering inks of other Examples and Comparative Examples were prepared by mixing and stirring ingredients including glittering particles, water, a water-soluble organic solvent and the like in the compositions and amounts (parts by weight) given in Tables 3 - 8 to disperse them, thereafter charging a water-soluble resin and filtering the resulting mixture, and subsequently degassing. In every preparation, heretofore known dispersing, degassing, filtering techniques and the like were used.

For information, a colored emulsion containing a fluorescent pigment is used as a colorant in Examples in Table 6.

Table 1 (Parts by weight)

		Examples					Comparative Examples	
		1	2	3	4	5	1	2
Glittering particles	①	7.0	–	7.0	–	–	–	–
	②	–	5.0	–	5.0	10.0	–	–
	⑤	–	–	–	–	–	5.0	–
	⑥	–	–	–	–	–	–	10.0
Water-soluble resin	①	0.3	0.3	–	–	–	0.3	–
	②	–	–	0.3	0.3	0.2	–	0.3
Colorant	①	1.0	1.0	–	–	–	–	–
	②	–	–	–	–	2.0	–	–
Pigment base	①	–	–	20.0	20.0	–	–	–
Water-soluble organic solvent	①	5.0	5.0	5.0	5.0	–	5.0	5.0
	②	–	–	–	–	7.0	–	–
	③	–	–	–	–	14.0	–	–
Antiseptic mildew-proofing agent	①	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Rust-inhibitor		0.1	0.1	0.1	0.1	0.1	0.1	0.1
Lubricant		1.2	1.2	1.2	1.2	1.2	1.2	1.2
Water		85.3	87.3	66.3	68.3	65.4	88.3	83.3
Evaluation test	Glittering feeling	○	○	○	○	○	×	×
	Spatial effect	○	○	○	○	○	×	×
	Writing performance	○	○	○	○	○	○	○

Table 2 (Parts by weight)

		Examples					Comparative Examples
		6	7	8	9	10	3
Glittering particles	⑦	7.0	–	7.0	–	7.0	–
	⑧	–	5.0	–	5.0	–	–
	①	–	–	–	–	–	7.0
Water-soluble resin	①	0.3	0.3	–	–	—	–
	②	–	–	0.3	0.3	0.2	0.3
	③	–	–	–	–	–	3.0
Water-soluble organic solvent	①	5.0	5.0	5.0	5.0	–	5.0
	②	–	–	–	–	7.0	–
	③	–	–	–	–	14.0	–
Colorant	②	–	–	–	–	2.0	–
Pigment base	②	–	–	–	–	–	40.0
Antiseptic mildew-proofing agent	①	0.1	0.1	0.1	0.1	0.1	0.1
Rust-inhibitor		0.1	0.1	0.1	0.1	0.1	0.1
Lubricant		1.2	1.2	1.2	1.2	1.2	1.2
Water		86.3	88.3	86.3	88.3	68.4	43.3
Evaluation test: Glittering feeling		○	○	○	○	○	×
Evaluation test: Writing performance		○	○	○	○	○	○

Table 3 (Parts by weight)

		Examples				
		11	12	13	14	15
Glittering particles	⑤	7.0	–	7.0	–	–
	④	–	5.0	–	5.0	10.0
Water-soluble resin	①	0.3	0.3	–	–	–
	②	–	–	0.3	0.3	0.2
Colorant	①	1.0	1.0	–	–	–
	②	–	–	–	–	2.0
Pigment base	①	–	–	20.0	20.0	–
Water-soluble organic solvent	①	5.0	5.0	5.0	5.0	–
	②	–	–	–	–	7.0
	③	–	–	–	–	14.0
Antiseptic mildew-proofing agent	①	0.1	0.1	0.1	0.1	0.1
Rust-inhibitor		0.1	0.1	0.1	0.1	0.1
Lubricant		1.2	1.2	1.2	1.2	1.2
Water		85.3	87.3	66.3	68.3	65.4
Evaluation test	Glittering feeling	○	○	○	○	○
	Spatial effect	○	○	○	○	○
	Writing performance	○	○	○	○	○

Table 4 (Parts by weight)

		Examples				Comparative Examples	
		16	17	18	19	4	5
Glittering particles	①	0.01	–	–	40.0	0.005	50.0
	④	–	0.5	30.0	–	–	–
Water-soluble resin	①	0.3	0.3	–	–	0.3	0.3
	②	–	–	0.3	0.3	–	–
Colorant	①	1.0	1.0	1.0	2.0	–	2.0
Water-soluble organic solvent	①	5.0	5.0	5.0	5.0	5.0	5.0
Antiseptic mildew-proofing agent	①	0.1	0.1	0.1	0.1	0.1	0.1
Rust-inhibitor		0.1	0.1	0.1	0.1	0.1	0.1
Lubricant		1.2	1.2	1.2	1.2	1.2	1.2
Water		92.29	91.8	92.3	51.3	93.295	41.3
Evaluation test	Glittering feeling	○	○	○	○	×	○
	Spatial effect	○	○	○	○	×	○
	Writing performance	○	○	○	○	○	×

Table 5 (Parts by weight)

		Examples				Comparative Examples	
		20	21	22	23	6	7
Glittering particles	③	0.01	–	–	40.0	0.005	50.0
	④	–	0.5	30.0	–	–	–
Water-soluble resin	①	0.3	0.3	–	–	0.3	0.3
	②	–	–	0.3	0.3	–	–
Water-soluble organic solvent	①	5.0	5.0	5.0	5.0	5.0	5.0
Antiseptic mildew-proofing agent	①	0.1	0.1	0.1	0.1	0.1	0.1
Rust-inhibitor		0.1	0.1	0.1	0.1	0.1	0.1
Lubricant		1.2	1.2	1.2	1.2	1.2	1.2
Water		93.29	92.8	63.3	53.3	93.295	43.3
Evaluation test	Glittering feeling	○	○	○	○	×	○
	Writing performance	○	○	○	○	○	×

Table 6 (Parts by weight)

		Examples						
		24	25	26	27	28	29	30
Glittering particles	①	5.0	5.0	–	–	–	–	–
	②	–	–	5.0	–	–	–	–
	③	–	–	–	5.0	–	–	–
	④	–	–	–	–	5.0	–	–
	⑦	–	–	–	–	–	5.0	–
	⑧	–	–	–	–	–	–	5.0
Water-soluble resin	①	0.3	0.3	–	–	–	0.3	–
	②	–	–	0.3	0.3	0.3	–	0.3
Colorant	⑤	1.0	–	1.0	1.0	–	1.0	1.0
	⑥	–	1.0	–	–	1.0	–	–
Water-soluble organic solvent	①	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Antiseptic mildew-proofing agent	①	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Rust-inhibitor		0.1	0.1	0.1	0.1	0.1	0.1	0.1
Lubricant		1.2	1.2	1.2	1.2	1.2	1.2	1.2
Water		87.3	87.3	87.3	87.3	87.3	87.3	87.3
Evaluation test	Glittering feeling	○	○	○	○	○	○	○
	Spatial effect	○	○	○	○	○	–	–
	Writing performance	○	○	○	○	○	○	○

Table 7 (Parts by weight)

		Examples			
		31	32	33	34
Glittering particles	①	7.0	–	7.0	–
	②	–	5.0	–	5.0
	⑤	–	–	–	–
	⑥	–	–	–	–
Water-soluble resin	④	0.3		–	0.2
	⑤	–	0.3		0.1
	⑥			0.3	
Colorant	①	1.0	1.0	–	–
	②	–	–	–	–
Pigment base	①	–	–	20.0	20.0
Water-soluble organic solvent	①	5.0	5.0	5.0	5.0
	②	–	–	–	–
	③	–	–	–	–
Antiseptic mildew-proofing agent	①	0.1	0.1	0.1	0.1
Rust-inhibitor		0.1	0.1	0.1	0.1
Lubricant		1.2	1.2	1.2	1.2
Water		85.3	87.3	66.3	68.3
Evaluation test	Glittering feeling	○	○	○	○
	Spatial effect	○	○	○	○
	Writing performance	○	○	○	○

Table 8 (Parts by weight)

		Examples					
		35	36	37	38	39	40
Glittering particles	①	5.0	5.0	5.0	–	–	–
	②	–	–	–	5.0	5.0	5.0
	⑤	5.0	–	–	5.0	–	–
	⑥	–	5.0	–	–	5.0	–
Water-soluble resin	①	0.3	0.3	0.3	0.3	0.3	0.3
Pigment base	③	–	–	20.0	–	–	20.0
Water-soluble organic solvent	①	5.0	5.0	5.0	5.0	5.0	5.0
Antiseptic mildew-proofing agent	①	0.1	0.1	0.1	0.1	0.1	0.1
Rust-inhibitor		0.1	0.1	0.1	0.1	0.1	0.1
Lubricant		1.2	1.2	1.2	1.2	1.2	1.2
Water		83.3	83.3	68.3	83.3	83.3	68.3
Evaluation test	Glittering feeling	○	○	○	○	○	○
	Spatial effect	○	○	○	○	○	○
	Writing performance	○	○	○	○	○	○

(Example 41)

An aqueous glittering ink of Example 41 was obtained in the composition and amounts (parts by weight) given in Table 9 by the following method of preparation with regard to compounding of the synthetic resin emulsion. That is, water, a water-soluble organic solvent and, as needed, other additives are mixed and stirred; glittering particles are charged to the resultant and stirred; and thereafter a water-soluble thickening resin is added and stirred. Next, the pH of the mixed liquid is adjusted as needed, and a colorant is added and stirred as needed. Subsequently, a synthetic resin emulsion is added and mixed.

In this preparation, heretofore known dispersing, degassing, filtering techniques and the like were adopted. In the foregoing producing process, the pH was adjusted to 8.5 with caustic soda.

(Examples 42 - 49)

Aqueous glittering inks of Examples 42 - 49 were prepared in the same manner as Example 41 except for using the compositions and amounts (parts by weight) given in Tables 9 and 10.

(Comparative Examples 8 - 14)

Aqueous glittering inks of Comparative Examples 8 - 14 were prepared in the same manner as Example 41 except for using the compositions and amounts (parts by weight) given in Tables 9 and 10.

For information, in Examples 42 - 49 and Comparative Examples 8 - 14 used, heretofore known dispersing, degassing, filtering techniques and the like were adopted.

Table 9 (Parts by weight)

		Examples					Comparative Examples		
		41	42	43	44	45	8	9	10
Glass flake particles	④	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Water-soluble thickening resin	④	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
	⑤	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Binder component (solids)	①	7.5							
	②		7.5						
	③			7.5					
	④				7.5				
	⑤					7.5			
	⑥							2.0	15.0
Water-soluble organic solvent	①	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
	④	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0
Pigment base	①	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Antiseptic mildew-proofing agent	①	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Lubricant		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Water		63.0	63.0	63.0	63.0	63.0	70.5	68.5	55.5
Fixability		○	○	○	○	○	×	×	○
Writing aptitude		○	○	○	○	○	○	○	×
Glittering feeling		○	○	○	○	○	○	○	○
Spatial effect		○	○	○	○	○	○	○	○

Note) The binder component is indicated by a content of solids (parts by weight).

Table 10 (Parts by weight)

		Examples				Comparative Examples			
		46	47	48	49	11	12	13	14
Glass flake particles	④	5.0	0.5	30	5.0	5.0	5.0	0.01	50
Water-soluble thickening resin	④	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
	⑤	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Binder component (solids)	①	40			0.01	0.005	45		
	②		7.5	7.5				7.5	7.5
Water-soluble organic solvent	①	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
	④	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0
Pigment base	①	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Antiseptic mildew-proofing agent	①	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Lubricant		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Water		30.5	67.5	38.0	70.49	70.495	25.5	67.99	18.0
Fixability		○	○	○	○	×	○	○	○
Writing aptitude		○	○	○	○	○	×	○	×
Glittering feeling		○	○	○	○	○	×	×	○
Spatial effect		○	○	○	○	○	×	×	○

Note) The binder component is indicated by a content of solids (parts by weight).

In Tables 1 - 10, each raw material composition is as follows:

(Glittering particles)

① Glass Flake Particles: Trade name "Crystal Color GF2525-M", manufactured by Toyo Aluminium Co., Ltd., median diameter = about 25 μm

② Glass Flake Particles: Trade name "Crystal Color GF2540", manufactured by Toyo Aluminium Co., Ltd., median diameter = about 40 μm

③ Glass Flake Particles: Trade name "Metashine REFSX-2025PS", manufactured by Toyo Aluminium Co., Ltd., median diameter = about 25 μm

④ Glass Flake Particles: Trade name "Metashine REFSX-2040PS", manufactured by Toyo Aluminium Co., Ltd., median diameter = about 40 μm

⑤ Aluminum powder: trade name "WXM0630", manufactured by Toyo Aluminium Co., Ltd., average particle size = about 5 μm

⑥ Pearlescent pigment: trade name "Iriodin 302", manufactured by Merck Japan Limited, average particle size = about 5 - 20 μm

⑦ Metal coated inorganic particles (yellow): trade name "Paliocrom Gold L2002", manufactured by BASF AG, median diameter = about 20 μm

⑧ Metal coated inorganic particles (yellow): trade name "Paliocrom Gold L2022", manufactured by BASF AG, median diameter = about 16 μm

(Water-soluble resin)

① Rhamsan gum: trade name "K7C233", manufactured by Sansho Co., Ltd

② Welan gum: trade name "K1C376", manufactured by Sansho Co., Ltd

③ Carboxymethyl cellulose (CMC): trade name "Cellogen 7A", number

average molecular weight = 27000 - 33000, manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.

④ Xanthan gum: trade name "Kelzan", manufactured by Kelco a unit of Monsanto Company.

⑤ Polyacrylic acid: trade name "Carbopol 940", manufactured by BF Goodrich Co., Ltd.

⑥ Succinoglycan: trade name "Reozan", manufactured by Sansho Co., Ltd

(Water-soluble organic solvent)

① Glycerin

② Dipropylene glycol monopropyl ether

③ Dipropylene glycol monomethyl ether

④ Propylene glycol

(Binder component / Fixing agent)

① Acrylic synthetic resin emulsion: trade name "Nikasol FX336", manufactured by Nihon Carbide Co., Ltd. ; anionic property; pH 7.5; minimum film forming temperature 0°C

② Vinyl acetate synthetic emulsion: trade name "Nikasol TG134A" manufactured by Nihon Carbide Co., Ltd. pH 7.5; minimum film forming temperature 0°C

③ Vinyl acetate synthetic emulsion: trade name "Mowinyl 507" manufactured by Clariant Polymer Co., Ltd. nonionic property; pH 6.5; minimum film forming temperature 0°C

④ Acrylic ester copolymer resin emulsion: trade name "Mowinyl DM772" manufactured by Clariant Polymer Co., Ltd. anionic property; pH 8.5; minimum film forming temperature 12~14℃

⑤ Acrylic ester copolymer resin emulsion: trade name "Mowinyl 700" manufactured by Clariant Polymer Co., Ltd. anionic property; pH 8.0; minimum film forming temperature 5℃

⑥ Methyl cellulose: trade name "Seska MC25S" manufactured by Daiichi Kogyo Seiyaku Co., Ltd.

(Colorant)

① Yellow dye: trade name "Yellow 202 (1)", Acid Yellow 73, Aizen Co., Ltd.

② Red dye: trade name "Chugai Aminol First pink R", xanthen-type, manufactured by Chugai Kasei Co., Ltd.

③ Blue pigment: trade name "Firstgen Blue TGR", phthalocyanine blue, manufactured by Dainippon Ink & Chemicals, Inc.

④ Yellow pigment: trade name "Seikafast Yellow A-3", azo-type, manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd.

⑤ Yellow resin emulsion: trade name "LUMIKOL NKW-2105", yellow fluorescent pigment, manufactured by Nippon Keiko Kagaku CO., Ltd.

⑥ Blue resin emulsion: trade name "LUMIKOL NKW-2108", blue fluorescent pigment, manufactured by Nippon Keiko Kagaku CO., Ltd.

⑦ White pigment: trade name "Kronos-KR380", titanium oxide, manufactured by Titan Kogyo CO., LTD.

(Pigment base)

① Pigment base: A pigment dispersion of a pigment base was obtained, in the form of a water dispersion of pigment (average particle size = 0.08 μm; solid content = 10% by weight), by adding and dissolving triethylamine to a mixture obtained by mixing the above-mentioned blue pigment ③ and the following resin for dispersing pigment in the following proportion, and thereafter conducting dispersion with a ball mill. As the resin for dispersing pigment a styrene-acryl copolymer was used (trade name "JOHNCRYL J683", Johnson Polymer Co., Ltd., weight average molecular weight = 8000).

Blue pigment ③	5 parts by weight
Resin for dispersing pigment	1 part by weight

② Pigment base: A pigment dispersion of a pigment base was obtained, in the form of a water dispersion of pigment (average particle size = 0.08 μm; solid content = 10% by weight), by adding and dissolving triethylamine to a mixture obtained by mixing the above-mentioned yellow pigment ④ and the following resin for dispersing pigment in the following proportion, and thereafter conducting dispersion with a ball mill. As the resin for dispersing pigment was used a styrene-acryl copolymer (trade name "JOHNCRYL J683", Johnson Polymer Co., Ltd., weight average molecular weight = 8000).

Yellow pigment ④	5 parts by weight
Resin for dispersing pigment	1 part by weight

③ Pigment base: A pigment dispersion of a pigment base was obtained, in the form of a water dispersion of pigment (average particle size =

0.4 μm; solid content = 10% by weight), by adding and dissolving triethylamine to a mixture obtained by mixing the above-mentioned white pigment ⑦ and the following resin for dispersing pigment in the following proportion, and thereafter conducting dispersion with a ball mill. As the resin for dispersing pigment is used a styrene-acryl copolymer (trade mane "JOHNCRYL J683", Johnson Polymer Co., Ltd., weight average molecular weight = 8000).

White pigment ⑦	5 parts by weight
Resin for dispersing pigment	1 part by weight

(Antiseptic mildew-proofing agent)

① 1,2-Benzoisothiazolin-3-one (trade name "Proxell GXL", Hoechst Synthesis Co., Ltd.)

(Rust-inhibitor)

Benzotriazole

(Lubricant)

Maleic monoamide

(Preparation of test samples)

Next, each of the inks of Examples and Comparative Examples given in Tables 1 - 10 was packed into an ink container made of a hollow polypropylene tube equipped with a ball-point pen tip made of stainless steel (ball material: silicon carbide), and ball-point pens of test samples having the ink containers therein were prepared. The diameter of a ball is 1.0mm.

(Evaluation test)

The glittering feeling and spatial effect of each ink for the Examples

and Comparative Examples given in Table 1 and the glittering feeling of each ink for the Examples and Comparative Examples given in Table 2 were evaluated by writing on commercially available loose-leaf sheets with these ball-point pens. The glittering feeling and spatial effect of each ink for the Examples and Comparative Examples given in Tables 3 - 4, the glittering feeling of each ink for the Examples and Comparative Examples given in Table 5, the glittering feeling and spatial effect of the ink for Example 28 given in Table 6 and the glittering feeling of each ink for Examples 29 and 30 given in Table 6 were evaluated. The glittering feeling and spatial effect of each ink wherein other water-soluble resins were incorporated were evaluated for Examples 31 - 34 given in Table 7. The glittering feeling and spatial effect of each ink were evaluated for Examples 35 - 40 given in Table 8. Also, the writing performance was evaluated for each Example and each Comparative Example given in Tables 1 - 8. The glittering feeling, spatial effect and furthermore fixability and writing aptitude were evaluated for each ink of Examples 41 - 49 containing resin emulsions given in Tables 9 and 10.

(Evaluation of glittering feeling)

Evaluation of the glittering feeling was conducted by visual observation of writings. Rating criteria were: ○ for ones having strong glittering feeling; × for ones having little or no glittering feeling.

(Evaluation of spatial effect)

Evaluation of the spatial effect also was conducted by visual observation. Rating criteria were: ○ for ones having spatial effect; × for

ones having no spatial effect.

(Evaluation of writing performance)

The writing performance was evaluated according to feeling in writing. Rating criteria were: ○ for ones having good writing performance and permitting smooth writing; × for ones having poor writing performance and not permitting smooth writing very much.

(Test of fixability)

The fixability shown in Tables 9 and 10 was evaluated according to the following criteria by writing on commercially available loose-leaf sheets with ball-point pens of test samples according to every Example and Comparative Example, drying the written marks, thereafter adhering commercially available adhesive cellophane tapes thereon, and then visually observing conditions after peeling the tapes.

- ○: Glittering particles remain on the written mark and the glittering feeling before peeling of the cellophane tape has not been lost.
- ×: Glittering particles are peeled from the written mark and the glittering feeling before peeling of the cellophane tape has been lost.

(Test of writing characteristics)

The writing characteristics shown in Tables 9 and 10 were evaluated by writing on commercially available loose-leaf sheets with ball-point pens of test samples according to every Example and Comparative Example, and rating writing feeling according to the following criteria.

- ○: Writing feeling is smooth.
- ×: Writing feeling is heavy and the ink does not flow. A double-line

written mark was obtained.

Tables 1 - 10 show results of glittering feeling, spatial effect and writing performance in each Example and each Comparative Example.

From Table 1, Examples 1 and 2 provided written marks having both a strong glittering feeling like sunshine and strong spatial effect. Examples 3 and 4 provided written marks having a strong glittering feeling like stars twinkling in the night sky and strong spatial effect. Example 5 provided coated films with a glittering feeling and spatial effect inside and a double-colored red written mark outside. On the other hand, Comparative Examples 1 and 2 provided written marks having weak glittering feeling but having no spatial effect. Writing performances of the inks of Examples 1 - 5 were good as in Comparative Examples 1 and 2.

From Table 2, Examples 6 - 9 containing metal coated inorganic particles as glittering particles provided golden written marks with strong glittering feeling. Likewise, Example 10 containing metal coated inorganic particles as glittering particles provided coated films having glittering feeling inside and a double-colored red written mark. On the other hand, Comparative Example 3 containing conventional aluminum powder particles as glittering particles provided a golden metallic written mark having poor and weak glittering feeling. Writing performances of the inks of Examples 6 - 10 were good as in Comparative Example 3.

The inks of Examples 1 - 5 containing glass flake particles can provide written marks with an unprecedented unique feeling since these inks can provide written marks with both a strong glittering feeling and strong spatial effect by comprising glass flake particles and colorants instead of

using glittering pigments as in Comparative Examples 1 - 2.

The inks of Examples 6 - 10 containing metallic coated inorganic particles as glittering particles cannot provide strong spatial effect but can provide written marks or coated films having a strong glittering feeling without loosing glitter in comparison to the ink of Comparative Example 3.

From Table 3, the inks of Examples 11 and 12 containing glass flake particles provided written marks having a strong glittering feeling like sunshine and strong spatial effect as in the inks of Examples 1 and 2. The inks of Examples 13 and 14 provided written marks having a strong glittering feeling like stars twinkling in the night sky and strong spatial effect as in the inks of Examples 3 and 4. The ink of Example 15 provided a glittering coated film inside and a double-colored red written mark outside as in the ink of Example 10. The inks of these Examples 11 - 15 were also good in writing performance.

From Table 4, the inks of Examples 16 - 19 containing glass flake particles in 0.01 - 40% by weight relative to the total amount of the inks provided good writing performances and also provided written marks having a strong glittering feeling and spatial effect. On the other hand, the ink of Comparative Example 4 containing glass flake particles in less than 0.01% by weight relative to the total amount of the ink did not provide a strong glittering feeling and the glittering feeling was poor and weak. Moreover, the ink of Comparative Example 4 also had a weak spatial effect which had been reduced. On the other hand, the ink of Comparative Example 5 containing glass flake particles in more than 40% by weight relative to the total amount of the ink had both strong glittering feeling and strong spatial

effect, but had poor writing characteristics.

From Table 5, the inks of Examples 20 - 23 containing metal coated inorganic particles as glittering particles in 0.01 - 40% by weight relative to the total amount of the inks provided good writing performances and also provided written marks having strong glittering feeling. On the other hand, the ink of Comparative Example 6 containing metal coated inorganic particles in less than 0.01% by weight relative to the total amount of the ink provided no strong glittering feeling and the glittering feeling was poor and weak. On the other hand, the ink of Comparative Example 7 containing metal coated inorganic particles in more than 40% by weight relative to the total amount of the ink had a strong glittering feeling, but had poor writing performance.

From Table 6, the inks of Examples 24 - 28 provided fluorescent written marks having a strong glittering feeling and spatial effect. The inks of Examples 29 and 30 provided fluorescent golden written marks having a strong glittering feeling. In the case of these inks, writing performance was also good.

From Table 7, also the inks of Examples 31 to 34 wherein water-soluble resins including xanthan gum, polyacrylic acid and succinoglycan are compounded provided written marks having a strong glittering feeling and spatial effect. Moreover, from Table 8, in the case of the inks of Examples 35 - 40 containing an aluminum powder pigment, titanium oxide and the like, the colors of the written marks were clearly shown up even on a black paper because of their sufficient opacifying power, and glittering written marks having a strong glittering feeling and spatial effect were obtained.

From Tables 9 and 10, the aqueous glittering ink of Examples 41 - 49 exhibited a glittering feeling suggestive of a jewel, aquamarine, and provided good fixability and good writing aptitude.

On the other hand, Comparative Example 8 provided a glittering feeling and spatial effect suggestive of a jewel, aquamarine, but no fixability was obtained at all. In Comparative Example 9, a glittering feeling and spatial effect suggestive of a jewel, aquamarine, provided and writing aptitude was good, but no fixability was obtained at all. Moreover, in Comparative Example 10, a glittering feeling and spatial effect suggestive of a jewel, aquamarine, provided and fixability was good, but writing performance was poor.

Furthermore, Table 10 shows that the inks of the Examples preferably contain the synthetic resin emulsions in 0.01 - 40% by weight in solids relative to the total amounts of the inks. It also shows that the inks of the Examples preferably contain the glass flake particles in 0.01 - 40% by weight relative to the total amounts of the inks.

Moreover, although each of the above-mentioned Examples applied the inks for those for ball-point pens, it can be used for other writing tools, printing inks, fields pertaining to coatings, to cosmetics, and the like.

Since the present invention is an aqueous glittering ink containing glass flake particles, a water-soluble resin, a water-soluble organic solvent and water, it can provide an unprecedented unique written mark or coated film having a glittering feeling and spatial effect stronger than that of aqueous ink using conventional glittering pigments. In particular, in the case of the foregoing aqueous glittering ink containing a colorant together

with glass flake particles, the strong glitter depending upon the hue of the colorant can be provided to written marks or coated films.

Furthermore, the aqueous glittering ink wherein metal coated inorganic particles are compounded as glittering particles and which contains, at least, a water-soluble resin, a water-soluble organic solvent and water can provide written marks or coated films having a strong glittering feeling without loosing glittering feeling in comparison to the aqueous ink using conventional glittering pigments. Moreover, in the case of the above-mentioned aqueous glittering ink containing a colorant together with metal coated inorganic particles, the strong glitter depending upon the hue of the colorant can be provided to written marks or coated films.

Moreover, the aqueous glittering ink containing glass flake particles, a water-soluble thickening resin, a water-soluble organic solvent and water as essential ingredients and containing a binder component, preferably a synthetic resin emulsion, for fixing the glass flake particles to written marks or coated films can improve fixability of the glass flake particles to the written mark or the coated film and can continue to provide a stronger glittering feeling and spatial effect to the written mark or the coated film without deteriorating ink characteristics or writing characteristics and without inhibiting effects of the compounding of the glass flake particles on the strong glittering feeling and spatial effect.

Next, as in the Examples and Comparative Examples shown in Tables 1 to 8, aqueous glittering inks of the Examples and Comparative Examples provided by mixing and stirring ingredients including water, a water-soluble organic solvent, glittering particles and a colorant or a pigment base and the

like in the compositions and amounts (parts by weight) given in Tables 11 to 13 to disperse them, thereafter charging a water-soluble resin and filtering the resulting mixture, and subsequently degassing. In every preparation, heretofore known dispersing, degassing, filtering techniques and the like were used.

Likewise, as in the Examples and Comparative Examples shown in Tables 9 and 10, aqueous glittering inks of other Examples and Comparative Examples were prepared by mixing and stirring ingredients including water, a water-soluble organic solvent, and, as required, other additives in the compositions and amounts (parts by weight) given in Tables 14 to 16 to stir them, charge glittering particles and stir, thereafter charging a water-soluble thickening resin and stirring the resulting mixture. Next, after adjusting the pH, as required, the colorants as required was added and stirred. Subsequently, synthetic resin emulsion was added and mixed. For information, in this preparation, heretofore known dispersing, degassing, filtering techniques and the like were used. By the pH adjustment in the said method of preparation, the pH was adjusted to 8.5 by caustic soda.

Table 11

(Parts by weight)

		Trade name		D_{50}	Example 50	51	52	53	54	55	56	57	58	59
Glittering Particles	Glass flake	REFS X	2015PS	15	5									
		REFS X	2025PS	25		5								
		REFS X	2040PS	40			5					5	5	
	Aluminum Powder	WXM	0630	5										
		WXM	U75C	13				5						
		WXM	5422	18					5					
		WXM	1440	30						5				5
		WXM	1415	50							5			
Fixing Agent		Nikasol FH-011A												
		Mowinyl DM772												
Colorant		Pigment base			1	1	1	1	1	1	1	5	10	6
Organic Solvent		Glycerine			7	7	7	7	7	7	7	7	7	7
		Propylene Glycol			15	15	15	15	15	15	15	15	15	15
Surfactant		Phosphanol PE-510			1	1	1	1	1	1	1	1	1	1
Thickening Resin		Kelzan			0.3	0.3	0.3					0.3	0.3	
		Carbopol			0.2	0.2	0.2					0.2	0.2	
		Reozan						0.3	0.3	0.3	0.3			0.3
Water					70.5	70.5	70.5	70.7	70.7	70.7	70.7	66.5	61.5	65.7
Median diameter (µm)					15	25	40	13	18	30	60	40	40	30
Smoothness (µm)					0.05	0.05	0.05	0.14	0.04	0.04	0.04	0.05	0.05	0.04
Smoothness/Median diameter					0.003	0.002	0.0013	0.011	0.0022	0.0013	0.0008	0.0013	0.0013	0.0013
Covering ratio of the colorants (%)					14	14	14	5	3	1	5	40	80	65
Interspersing rate of the glittering particles (%)					30	30	30	45	40	33	25	30	30	33
Concavo-convex degree of the resin coating (µm)					–	–	–	–	–	–	–	–	–	–
Smoothness on the coated films (µm)					9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2
Viscosity(mPa·s)		$V_{0.5}$(rotation speed 0.5rpm)			6000	6500	7200	6000	5400	8600	6500	7000	8600	5400
		T.I.Value($V_{0.5}$/$V_{1.0}$)			1.7	1.7	1.7	1.9	1.9	1.8	1.8	1.7	1.7	1.9
Color development					◎	◎	◎	◎	◎	◎	◎	◎	◎	◎
Glittering feeling					○	◎	◎	○	○	◎	◎	◎	○	○
Writing performance		Initial writing performance (writing performance right after constructing the pen)			○	○	○	○	○	○	○	○	○	○
		Writing performance three days after directing the pen tip downward			○	○	○	○	○	○	○	○	○	○

Table 1 2

(parts by weight)

		Trade name		D_{50}	Example 60	61	62	63	64	65	66	67	68	69	70	71
Glittering particles	Glass Flake	REFSX	2015PS	15												
		REFSX	2025PS	25												
		REFSX	2040PS	40		1	3	15	28					5	5	5
	Aluminum Powder	WXM	0830	5												
		WXM	U75C	13												
		WXM	5422	18												
		WXM	1440	30	5					1	3	10	20			
		WXM	1415	50												
Fixing Agent		Nikasol FH-011A														
		Mowinyl DM772														
Colorant		Pigment base			8	1	1	1	1	1	1	1	1	1	1	1
Organic Solvent		Glycerins			7	7	7	7	7	7	7	7	7	7	7	7
		Propylene glycol			15	15	15	15	15	15	15	15	15	15	15	15
Surfactant		PhosphanolPE-510			1	1	1	1	1	1	1	1	1	1	1	1
Thickening resin		Kelzan				0.3	0.3	0.3	0.3					0.18	0.14	0.6
		Carbopol				0.2	0.2	0.2	0.2					0.09	0.06	0.3
		Reezan			0.3					0.3	0.3	0.3	0.3			
Water					63.7	74.5	72.5	80.5	47.5	74.7	72.7	65.7	55.7	70.73	70.8	70.1
Median diameter (μm)					30	40	40	40	40	30	30	30	30	40	40	40
Smoothness (μm)					0.04	0.05	0.05	0.05	0.05	0.04	0.04	0.04	0.04	0.05	0.05	0.05
Smoothness/Median diameter					0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013
Coating ratio of the colorants (%)					80	25	14	14	14	10	1	1	1	14	14	14
Interspersing rate of the glittering particles (%)					33	12	24	50	80	13	26	60	78	30	30	30
Concavo-convex rate of coating resin (μm)					–	–	–	–	–	–	–	–	–	–	–	–
Smoothness on the coated films (μm)					9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2
Viscosity (mPa·s)	$V_{0.5}$(rotation speed 0.5rpm)				5500	6200	7000	7600	8200	5600	6300	7000	8000	2100	1000	14000
	T.I.Value ($V_{0.5}/V_{10}$)				1.8	1.7	1.7	1.7	1.7	1.8	1.8	1.8	1.8	1.6	1.6	1.7
Color development					◎	◎	◎	○	○'	◎	◎	○	○'	◎	◎	◎
Glittering feeling					○	○	◎	◎	◎	○	◎	◎	◎	◎	◎	◎
Writing performance	Initial writing performance (writing performance right after constructing the pen)				○	○	○	○	○	○	○	○	○	○	○	○
	Writing performance three days after directing the pen tip downward				○	○	○	○	○	○	○	○	○	○	○	○

Table 1 3

(parts by weight)

		Trade name	D_{50}	Comparative Examples										
				15	16	17	18	19	20	21	22	23	24	25
Glittering particles	Glass Flake	REFSX 2015PS	15											
		REFSX 2025PS	25											
		REFSX 2040PS	40		5	5		30	40			5	5	5
	Aluminum powder	WXM 0630	5	5										
		WXM U75C	13											
		WXM 5422	18											
		WXM 1440	30				5			30	40			
		WXM 1415	50											
Fixing Agent		Nikasol FH-011A												
		Mowinyl DM772												
Colorant		Pigment base		1	13	15	10	1	1	1	1	1	1	1
Organic solvent		Glycerine		7	7	7	7	7	7	7	7	7	7	7
		Propylene Glycol		15	15	15	15	15	15	15	15	15	15	15
Surfactant		Phosphanol PE-510		1	1	1	1	1	1	1	1	1	1	1
Thickening resin		Kelzan			0.3	0.3		0.3	0.3	0.3	0.3	0.3	0.09	0.7
		Carbopol			0.2	0.2		0.2	0.2	0.2	0.2	0.2	0.04	0.4
		Rezsan		0.3			0.3							
Water				70.7	58.5	56.5	61.7	45.5	35.5	45.5	35.5	70.5	70.9	69.9
Median diameter (μm)				5	40	40	30	40	40	80	80	40	40	40
Smoothness (μm)				0.14	0.05	0.05	0.04	0.05	0.05	0.04	0.04	0.05	0.05	0.05
Smoothness/Median diameter				0.028	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013
Coating ratio of the colorants (%)				10	92	100	100	14	14	1	1	14	14	14
Interspersing rate of the glittering particles (%)				100	30	30	33	85	100	95	100	30	30	30
Concavo-convex rate of the coating resin (μm)				–	–	–	–	–	–	–	–	–	–	–
Smoothness on the coated films (μm)				9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	5.9	9.2	9.2
Viscosity (mPa·s)	V_{05} (rotation speed 0.5rpm)			6500	7000	7000	5600	8200	40000	8000	40000	7200	550	25000
	T.I.Value (V_{05}/V_{1})			1.8	1.7	1.7	1.8	1.7	1.8	1.8	1.8	1.7	1.8	1.8
Color development				◎	◎	◎	◎	△	×	△	×	◎	◎	◎
Glittering feeling				×	△	×	×	◎	◎	◎	◎	×	◎	◎
Writing performance	Initial writing performance (writing performance right after constructing the pen)			○	○	○	○	○	×	○	×	○	○	×
	Writing performance three days after directing the pen tip downward			○	○	○	○	○	–	○	–	○	× (thin spot)	–

Table 1 4

(parts by weight)

					Example										
		Trade name		D_{50}	72	73	74	75	76	77	78	79	80	81	82
Glittering particles	Glass Flake	REFSX	2015PS	15	5										
		REFSX	2025PS	25		5									
		REFSX	2040PS	40			5					5		1	3
	Aluminum Powder	WXM	0630	5											
		WXM	U75C	13				5							
		WXM	5422	18					5						
		WXM	1440	30						5			5		
		WXM	1415	50							5				
Fixing Agent		Nikasol FH-011A													
		Mowinyl DM772			10	10	10	10	10	10	10	10	10	10	10
Colorant		Pigment base			1	1	1	1	1	1	1	5	5	1	1
Organic Solvent		Glycerine			7	7	7	7	7	7	7	7	7	7	7
		Propylene Glycol			15	15	15	15	15	15	15	15	15	15	15
Surfactant		Phosphanol PE-510			1	1	1	1	1	1	1	1	1	1	1
Thickening resin		Kelzan			0.3	0.3	0.3					0.3		0.3	0.3
		Carbopol			0.2	0.2	0.2					0.2		0.2	0.2
		Reozan						0.3	0.3	0.3	0.3		0.3		
Water					60.5	60.5	60.5	60.7	60.7	60.7	60.7	58.5	58.7	84.5	82.5
Median diameter (μm)					15	25	40	13	18	30	50	40	30	40	40
Smoothness (μm)					0.05	0.05	0.05	0.14	0.04	0.04	0.04	0.05	0.04	0.05	0.05
Smoothness/Median diameter					0.0033	0.002	0.0013	0.0108	0.0022	0.0013	0.0008	0.0013	0.0013	0.0013	0.0013
Coating (%)					14	14	14	5	3	1	5	80	75	25	14
Interspersing rate of the glittering particles (%)					30	30	30	45	40	33	25	30	33	12	24
Concavo-convex rate of the coating resin (μm)					0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Smoothness on the coated films (μm)					9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2
Viscosity(mPa·s)	$V_{0.5}$(rotationspeed: 0.5rpm)				6000	6500	7200	8000	5400	6600	6500	7000	5500	6200	7000
	T.I.Value($V_{0.5}/V_{10}$)				1.7	1.7	1.7	1.9	1.9	1.8	1.8	1.7	1.8	1.7	1.7
Color development					◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎
Glittering feeling					○'	○	○	○'	○'	○	○	○'	○'	○'	○
Flexability					○	○	○	○	○	○	○	○	○	○	○
Writing performance	Initial writing performance (writing performance right after constructing the pen)				○	○	○	○	○	○	○	○	○	○	○
	Writing performance three days after directing the pen tip downward				○	○	○	○	○	○	○	○	○	○	○

Table 1 5

(parts by weight)

		Trade name	D_{50}	Example 83	84	85	86	87	88	89	90	91	92	93	94
Glittering particles: Glass flake	REFSX	2015PS	15												
	REFSX	2025PS	25												
	REFSX	2040PS	40	15	28										
Glittering particles: Aluminum powder	WXM	0630	5												
	WXM	U75C	13												
	WXM	5422	18												
	WXM	1440	30			1	3	10	20						5
	WXM	1415	50												
Fixing Agent	Nikasol FH-011A									20	20	20	20	20	20
	Mowinyl DM772			10	10	10	10	10	10						
Colorant	Pigment base			1	1	1	1	1	1	1	1	5	5	10	5
Organic solvent	Glycerine			7	7	7	7	7	7	7	7	7	7	7	7
	Propylene glycol			15	15	15	15	15	15	15	15	15	15	15	15
Surfactant	Phosphanol PE-510			1	1	1	1	1	1	1	1	1	1	1	1
Thickening resin	Kelzan			0.3	0.3					0.3		0.3		0.3	
	Carbopol			0.2	0.2					0.2		0.2		0.2	
	Reczan					0.3	0.3	0.3	0.3		0.3		0.3		0.3
Water				50.5	37.5	54.7	52.7	55.7	45.7	50.5	50.7	46.5	46.7	41.5	43.7
Median diameter (μm)				40	40	30	30	30	30	40	50	40	50	40	50
Smoothness (μm)				0.05	0.05	0.04	0.04	0.04	0.04	0.05	0.04	0.05	0.04	0.05	0.04
Smoothness/Median diameter				0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0008	0.0013	0.0008	0.0013	0.0008
Coating ratio of the colorants (%)				14	14	10	1	1	1	14	1	40	70	80	80
Interspersing rate of the glittering particles (%)				50	80	13	28	60	73	30	33	30	33	30	33
Concavo-convex rate of the coating resin (μm)				0.25	0.25	0.25	0.25	0.25	0.25	0.15	0.13	0.15	0.13	0.15	0.13
Smoothness on the coated film (μm)				9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2
Viscosity (mPa·s)	V_{05} (rotation speed 0.5rpm)			7500	8200	5600	6300	7000	7500	7200	6600	7200	6600	7200	6600
	TI.Value (V_{05}/V_{1m})			1.7	1.7	1.7	1.7	1.8	1.8	1.8	1.7	1.7	1.8	1.7	1.8
Color development				○	○'	◎	◎	○	○'	◎	◎	◎	◎	◎	◎
Glittering feeling				○	○	○'	○	○	○	◎	◎	◎	○	○	○
Fixability				○	○	○	○	○	○	○	○	○	○	○	○
Writing performance	Initial writing performance (writing performance right after constructing the pen)			○	○	○	○	○	○	○	○	○	○	○	○
	Writing performance three days after directing the pen tip downward			○	○	○	○	○	○	○	○	○	○	○	○

Table 16

(Parts by weight)

			Trade name	D_{50}	Comparative Example								
					26	27	28	29	30	31	32	33	34
Glittering particles	Glass Flake	REFSX	2015PS	15									
		REFSX	2025PS	25									
		REFSX	2040PS	40		5	5		30	40			5
	Aluminum Powder	WXM	0830	5	5								
		WXM	U75C	13									
		WXM	5422	18									
		WXM	1440	30				5			30	40	
		WXM	1415	50									
Fixing Agent		Nikasol FH-011A											
		Mowinyl DM772				10	10	10	10	10	10	10	10
Colorant		Pigment base			1	10	15	10	1	1	1	1	1
Organic Solvent		Glycerine			7	7	7	7	7	7	7	7	7
		Propylene glycol			15	15	15	15	15	15	15	15	15
Surfactant		Phosphanol PE-510			1	1	1	1	1	1	1	1	1
Thickening resin		Kelzan				0.3	0.3		0.3	0.3	0.3	0.3	0.3
		Carbopol				0.2	0.2		0.2	0.2	0.2	0.2	0.2
		Reozan			0.3			0.3					
Water					60.7	51.6	46.5	51.7	35.5	25.5	35.5	25.5	60.6
Median diameter (D50) (μm)					5	40	40	30	40	40	30	30	40
Smoothness (μm)					0.14	0.05	0.05	0.04	0.05	0.05	0.04	0.04	0.05
Smoothness/Median diameter					0.028	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013
Coating ratio of the colorants (%)					10	93	100	100	14	14	1	1	14
Interspersing rate of the glittering particles (%)					100	30	30	33	85	100	95	100	30
Concavo-convex rate of the (μm)					0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Smoothness on the coated film (μm)					9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	6.9
粘度(mPa·s)	$V_{0.5}$(rotation speed 0.5rpm)				6500	7000	7000	5600	8200	40000	8000	40000	7200
	T.I.Value($V_{0.5}/V_{5.0}$)				1.8	1.8	1.7	1.8	1.7	1.8	1.8	1.8	1.7
Color development					◎	◎	◎	◎	△	×	△	×	◎
Glittering feeling					×	△	×	×	◎	◎	◎	◎	×
Fixability					○	○	○	○	○	○	○	○	○
Writing performance	Initial writing performance (writing performance right after constructing the pen)				○	○	○	○	○	×	○	×	○
	Writing performance three days after directing the pen tip downward				○	○	○	○	○	–	○	–	○

In Tables 11 - 16, each raw material composition is as follows:

(Glittering particles)

① Glass Flake Particles: trade name "Metashine REFSX-2015PS", manufactured by Toyo Aluminium Co., Ltd., median diameter = about 15 μm

② Glass Flake Particles: trade name "Metashine REFSX-2025PS ", manufactured by Toyo Aluminium Co., Ltd., median diameter = about 25 μm

③ Glass Flake Particles: trade name "Metashine REFSX-2040PS", manufactured by Toyo Aluminium Co., Ltd., median diameter = about 40 μm

④ Aluminum powder: trade name "WXM0630", manufactured by Toyo Aluminium Co., Ltd., median diameter = about 5 μm

⑤ Aluminum powder: trade name "WXM U75C", manufactured by Toyo Aluminium Co., Ltd., average particle size = about 13 μm

⑥ Aluminum powder: trade name " WXM 5422", manufactured by Toyo Aluminium Co., Ltd., average particle size = about 18 μm

⑦ Aluminum powder: trade name " WXM 1440", manufactured by Toyo Aluminium Co., Ltd., average particle size = about 30 μm

⑧ Aluminum powder: trade name "WXM 1415", manufactured by Toyo Aluminium Co., Ltd., average particle size = about 50 μm

(Water-soluble resin)

① Xanthan gum: trade name "Kelzan", manufactured by Kelco a unit of Monsanto Company.

④ Polyacrylic acid: trade name "Carbopol 940", manufactured by BF Goodrich Co., Ltd.

⑤ Succinoglycan: trade name "Reozan", manufactured by Sansho Co.,

Ltd

(Water-soluble organic solvent)

① Glycerin

② Propylene glycol

(Binder component / Fixing agent)

① Acryl acrilate, Acryl methylacrilate ether copolymer resin emulsion: trade name "Nikasol FH-011A" , manufactured by Nihon Carbide Kogyo Co., Ltd. ; anionic property; pH 7.0; minimum film forming temperature 0°C; viscosity 150mPa · s (a BH-typed viscometer at the temperature of 25°C) ; median diameter = about 0.05 μm

② Acrylate ester copolymer resin emulsion: trade name " Mowinyl DM772" manufactured by Clariant Polymer Co., Ltd. ; anionic property, pH 8.5 ; minimum film forming temperature 12~14°C; viscosity 1200mPa · s (a BH-typed viscometer at the temperature of 25°C) ; median diameter = about 0.06 μm

Here, in the Tables, binder component/fixing agent is represented by the amount in which solids are contained.

(Colorant)

(Pigment base)

Pigment dispersion was prepared (average particle size = 0.08 μm; solid content = 10% by weight), by adding and dissolving sodium hydroxide to a mixture obtained by mixing phthalocyanine blue (5 parts by weight) and a styrene-acryl copolymer (1 part by weight: trade name "JOHNCRYL J683", Johnson Polymer Co., Ltd., weight average molecular weight = 8000)

thereafter conducting dispersion with a ball mill.

(Lubricant / Surfactant)

mono (di) polyoxyethylene alkyl ether phospholate: manufactured by Toho Kagaku Kogyo Co., Ltd. under the trade name of "Phosphanol PE-510"

(Preparation of test samples)

Next, a ball point pen was prepared for each sample test wherein each of the ink of Examples and Comparative Examples given in Table 11-16 was packed into an ink container made of a hollow polypropylene tube equipped with a ball-point pen tip made of stainless steel (ball material: silicon carbide), and ball-point pens of test samples having the ink containers therein were prepared. The diameter of a ball is 1.0mm.

(Evaluation Test)

The glittering feeling and color development of each ink for the Examples and Comparative Examples given in Tables 11 to 16 were evaluated in a state of dried written marks by writing on commercially available loose-leaf sheets with these ball-point pens. The fixability of the written marks or coated films of the ink was also evaluated in Tables 14 to 16. In addition, the viscosity and thixotropy index (T.I. value) in each of the Examples and Comparative Examples were measured.

Here, in Tables 11 to 16, each property value is evaluated in a state of dried written marks. The said "median diameters" refers to D_{50} value (μm) measured by the method of laser diffraction analysis using an equipment manufactured by ELIONIX INC. under the trade name of "ERA-8000". In addition, the said smoothness is the average value of R_{max} (μm), the maximum value of roughness measured on each surface of the several

glittering particles which exist per unit area of the written marks or coated films in a state of dryness by using the microscope manufactured by ELIONIX INC. under the trade name of "ERA-8000 ".

Here, the "surface coating ratio of the colorant" refers to the coating ratio of the colorant including the coloring pigment which covers the surface of a particle and is represented by the coating area of the colorant to the total surface area of the surface of a particle. In the present invention, the coating ratio of the colorant is so obtained as using the electron microscope manufactured by ELIONIX INC. under the trade name of "ERA-8000" as already mentioned, and measuring the average value of the surface area of the said particles and the coating area of the colorant . "Interspersing rate" of the glittering particles refers to the value (%) obtained by measuring the area of the glittering particles occupying the total written surface by using the microscope manufactured by ELIONIX INC. under the trade name of "ERA-8000" as already mentioned, thereby calculating the ratio. The concavo-convex rate of the resin coated films refers to the average value of R_{max} (μm), the maximum value of roughness measured on each surface of the several glittering particles which exist per unit area of the written marks or coated films in a state of dryness by using the microscope manufactured by ELIONIX INC. under the trade name of "ERA-8000". Here, the "smoothness on the coated films" refers to the average value of R_{max} (μm), the maximum value of roughness measured on each surface of the several glittering particles which exist per unit area of the written marks or coated films in a state of dryness by using the microscope manufactured by ELIONIX INC. under the trade name of "ERA-8000".

Here, the Comparative Example 32 in the Table 16, the evaluation is conducted by writing on a commercially available art paper unlike the case of the said Examples and Comparative Examples using a commercially available loose-leaf sheet.

As for the ink viscosity, with the use of an ELD-typed viscometer obtained by Toki Sangyo Co., Ltd. the thixotropy index (T.I. value) is measured represented by the ratio of $V_{0.5}$ to $V_{1.0}$ ($V_{0.5}$ / $V_{1.0}$), wherein $V_{0.5}$ is the viscosity with the rotation speed of 0.5 rpm and $V_{1.0}$ is the viscosity with the rotation speed of 1.0 rpm when the ink is measured by the said ELD-typed viscometer (3° R14 cone, at the temperature of 20℃). The above tables also show the $V_{0.5}$, the viscosity when measured by an ELD-typed viscometer with a rotation speed of 0.5rpm(3° R14 cone at the temperature of 20℃).

(Evaluation of color development)

Evaluation of the color development was conducted by visual observation of writings. Rating criteria were, in a state of dried written marks, : ◎ for ones having particularly strong color development, ○ for ones having strong color development, ○' for ones having color development, △ for ones having little color development, × for ones having no color development.

(Evaluation of glittering feeling)

Evaluation of the glittering feeling was conducted by visual observation of writings. Rating criteria were, in a state of dried written marks,: ◎ for

ones having particularly strong glittering feeling, ○ for ones having strong glittering feeling, ○' for ones having glittering feeling, △ for ones having little color development, × for ones having no color development.

(Evaluation of fixability)

The fixability was evaluated according to the following criteria by writing on commercially available loose-leaf sheets with ball-point pens of test samples according to every Example and Comparative Example, drying the written marks, thereafter adhering commercially available adhesive cellophane tapes thereon, and then visually observing conditions after peeling the tapes.

○: Glittering particles remain on the written marks and the glittering feeling before peeling of the cellophane tape has not been lost.

×: Glittering particles are peeled from the written marks and the glittering feeling before peeling of the cellophane tape has been lost.

Tables 11 to 16 show the result of the glittering feeling and color development of the written marks or coated films of the ink according to every Example and Comparative Example. In addition, tables 14 to 16 show the result of the fixability of the said written marks or coated films.

(Evaluation of writing performance)

Writing performance refers to the one right after the construction of a ball-point pen in the said each test sample and the one three days after directing the pen-tip of the said ball-point pen downward. This writing performance was, as above-mentioned, evaluated based on the following

criteria, that is; ○ for ones having good writing performance with smooth feeling when writing and × for ones having poor writing performance with little smoothness. Further, in the Tables, those with thin spots are shown as ×(thin spots).

As shown in the Examples 50 to 56, Comparative Example 15, Example 72 to 78 and Comparative Example 26 in the Tables 11 to 16, it is recognized for the glittering particles to have a median diameter of at least 10μm further at least 13μm, preferably not less than 25μm, and most preferably not less than 30μm.

As shown in the Example 53, Comparative Example 15, Example 75 and Comparative Example 26 and the like in the Tables 11 to 16, it is recognized that the scaly glittering particles preferably have a ratio of smoothness on the particle surface to a median diameter of not greater than 0.011 in respect of the glittering feeling.

In addition, as shown in each of the Examples and Comparative Examples, that is, in the Examples 58, 57, 60, the Comparative Examples 16, the Examples 79, 84, Comparative Example 30 and the like in the Tables 11 to 16, it is recognized that the particles having the surface coating ratio of the said colorant on the said particle surface of not greater than 80% preferably not greater than 40% in a state of dried written marks are preferable.

In addition, it is recognized that the ink having the pseudo-plasticity fluidity (thixotropic property) with the said thixotropy index (T.I. value) of not less than 1.3 represented by the ratio of $V_{0.5}$ to $V_{1.0}$ ($V_{0.5}$ / $V_{1.0}$), wherein $V_{0.5}$ is the viscosity with the rotation speed of 0.5 rpm and $V_{1.0}$ is the

viscosity with the rotation speed of 1.0 rpm when the ink is measured by an ELD-typed viscometer (3° R14 cone, at the temperature of 20°C) and with $V_{0.5}$ of 1000~15000mPa · s, the viscosity when measured by an ELD-typed viscometer with a rotation speed of 0.5rpm(3° R14 cone at the temperature of 20°C) is desirable.

Moreover, as shown in each of the Examples and Comparative Examples, that is, in the Examples 64,84,63, and in the Comparative Examples 19,28~31 in the Tables 11 to 16, it is recognized that the written mark which intersperses this scaly glittering particles to the total written surface with the range of not greater than 80%, preferably within the range of 20~45% is good in respect of color development and glittering feeling.

Further, as shown in each of the Examples and Comparative Examples in the Tables 11 to 16, it is recognized that the concavo-convex rate which the resin film covers the surface of the scaly glittering particles not greater than 0.15μm is excellent in glittering feeling. It was also recognized to be preferable to have the smoothness of the coated films which is not less than 9μm.

Here, the present invention includes the identical subject matter disclosed in the specification, claims of Japanese Patent applications No.11-76868, No.11-360187, No.2000-2370 and No.2000-2344 to which is claimed priority for the present application.